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A Study on the Curing Process as the Compositizing Properties

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In this paper we describe an experimental study on changes of various mechanical properties especially in corrosion atmosphere, appearance of fracture, breaking state, changes of physical quantities, etc. regarding the curing process as the compositizing properties.

As a result of this series of tests and experiments, it was found that a good composite body from the view points of properties, productivity and economy can be made through curing temperature of 70°C and curing time of 1 hore.

With regard to compositizing properties, over-curing was better and on the safer side than under-curing, but overcuring beyond the pertinent curing conditions did not make a contribution to betterment of properties.

1. Introduction

Correlation can be found between curing and compositizing properties of FRP. If we may call it molding design, appropriate curing which fits the purpose of FRP might be one of the requisites for FRP. Changes of various mechanical properties especially in corrosion atmosphere, appearance of fracture, breaking state, changes of physical quantities, etc. are investigated experimentally in this article, regarding the curing process as the compositizing properties.[1),2)]

2. Experimental Method

Polyestel made by Japan Catalytic Chemical Industry Co., Ltd., "EPOLAC" N-150 AL, and glass fiber by Nitto Boseki Co., Ltd., "CHOPPED STRAND MAT" EMC-450, were used for experiments. Specimens of 3-ply mat, prepared by hand lay-up method, were hardened to satisfy the curing conditions shown in Table 1, thence test pieces as shown in Fig. 1 were made therefrom. Tension test was carried out

*Dep. of Textile Eng.

Table 1. Curing conditions.

	Curing temperature (°C)								
	0	5	10	20	30	40	70	100	130
Curing time (hr)	1	1	1	1	1	1	1	1	1
	3	3	3	3	3	3	3	3	3
	5	5	5	5	5	5	5	5	5
	7	7	7	7	7	7	7	7	7

using Autograph IS-2000 and in accordance with JIS K 6919-1970, and stress, strain, elastic modulus and absorbed energy were measured with all the specimens prepared under different curing conditions. Hardness test was carried out by Shore hardness tester with the specimens hardened under the conditions of Table. 1. In order to carry out tension test in relation to chemical resistance[3], test pieces as shown in Fig. 2 were prepared immediately after 1 hour of curing under curing temperature of 30°C, and those test pieces were subjected to tension test under 20°C and 65% RH in (1) atmosphere, (2) 10% NaOH, (3) 30% H_2SO_4 and (4) 95% $(CH_3)_2CO$, and 0, 1, 3, 5, 7, 14, 24, 48, 72, 96, 120, 144, 168, 336, 504 and 672 hours after preparing of said test pieces. For the purpose of hardness test in relation to chemical resistance, test pieces of 50 ± 1mm long and 50 ± 1mm wide were prepared immediately after 1 hour of curing under curing temperature of 30°C, and Shore hardness of such test pieces were measured under 20°C and 65% RH, in the same 4 conditions as in the case of tension test, and 0, 1, 3,····· 504, 672 and 1,008 hours after preparation. Test pieces for chemical resistance test of 50 ± 1mm long and 50 ± 1mm wide were prepared after curing under the condition of Table 1 and in accordance with JIS K 7114-1972. Those test pieces were then settled down for 7 days under 20 ± 1°C, in the chemicals identified as (2), (3) and (4) in the tension test above, and change in their size and weight were measured.

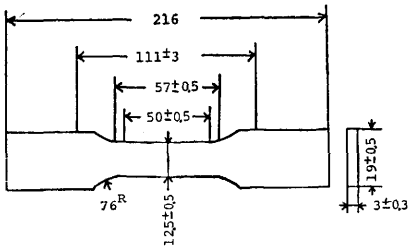


Fig. 1 Test piece for tension test.

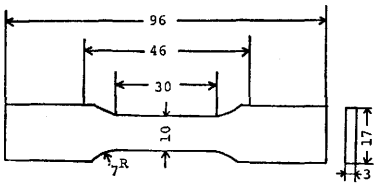


Fig. 2 Test piece for chemical resistance.

The following calculation method can be made.

Experimental condition: 20°C, 65% RH, 7 days passed

Fluctuating ratio of weight:

$$M\ (\%)=\frac{M_2-M_1}{M_1}\times 100$$

$$M'\ (\%) = \frac{M_2 - M_3}{M_1} \times 100$$

where, M, M' : fluctuating ratio of weight (%)

M_1 : weight of test piece on ordinary state (g)

M_2 : weight of test piece after experiment (g)

M_3 : weight of controled (20°C, 65% RH, 48 hr passed) test piece after experiment (g)

Fluctuating ratio of length:

$$L\ (\%) = \frac{l_2 - l_1}{l_1} \times 100$$

where, L : fluctuating ratio of length (%)

l_1 : length of test piece on ordinary state (mm)

l_2 : length of test piece after experiment (mm)

Fluctuating ratio of thickness:

$$T\ (\%) = \frac{t_2 - t_1}{t_1} \times 100$$

where, T : fluctuating ratio of thickness (%)

t_1 : thickness of test piece on ordinary state (mm)

t_2 : thickness of test piece after experiment (mm)

3. Experimental Results and Consideration

Changes of mechanical properties of FRP during the process of curing are shown in Figs. 3-7, from which it is known that the tensile strength becomes greater as the curing temperature goes up to 70°C, and it does not change any more when the temperature exceeds 70°C. It was also known that, when the curing time was longer than 1 hour, the fixed tensile strength was mostly 9.5 kg/mm², with very little flu-

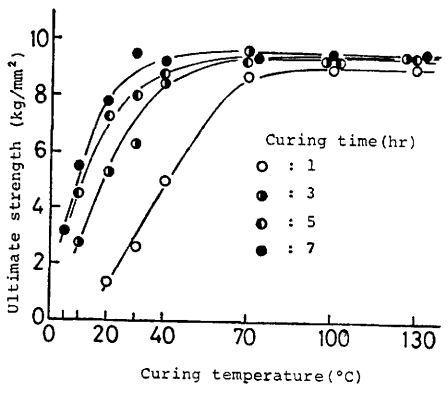


Fig. 3 Changes of mechanical properties of FRP during the process of curing.

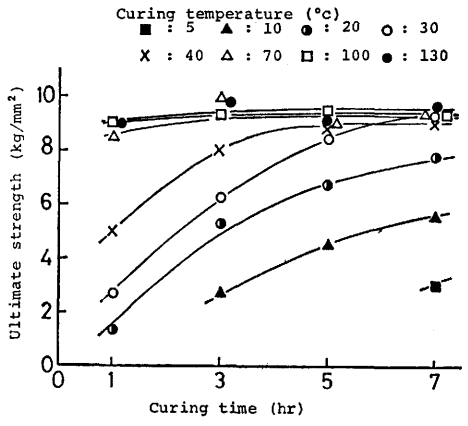


Fig. 4 Changes of mechanical properties of FRP during the process of curing.

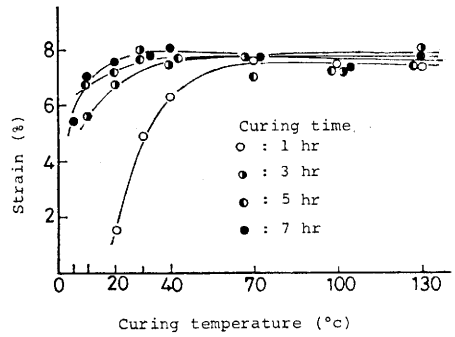


Fig. 5 Changes of mechanical properties of FRP during the process of curing.

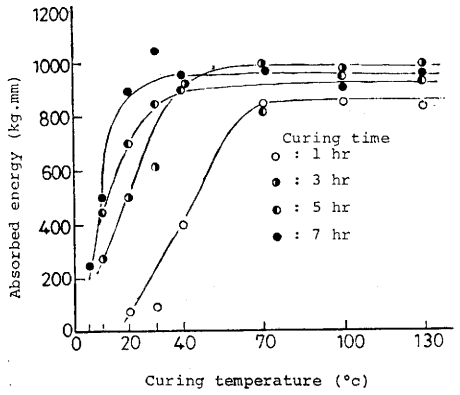


Fig. 7 Changes of mechanical properties of FRP during the process of curing.

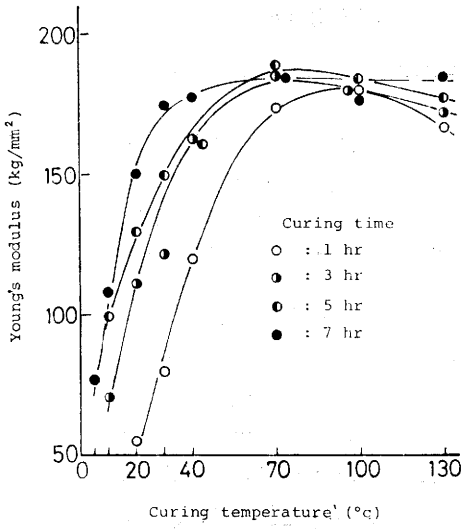


Fig. 6 Changes of mechanical properties of FRP during the Process of curing.

ctuation. Having a border at 70°C, tensile strength becomes greater as the curing time becomes longer if the temperature is lower than this 70°C, while strength shows the maximum value irrespective of the curing time when the temperature is more than 70°C. No compositization was found when the curing temperature was 5°C and the curing time was less than 7 hours. With regard to strain, the value at the time of breaking was constant when the curing temperature was more than 70°C, and no difference was observed in the strain value if the curing time was longer than 1 hour. Quite identical phenomenon was found in elastic modulus as well. Elastic modulus became greater as the curing temperature was longer until the curing temperature reached 70°C, but showed the fixed value irrespective of the curing time when the temparature exceeded 70°C. Absorbed energy was constant as well, within the range of 900–1,000 kg • mm when the temperature was higher than 70°C, irrespective of the curing time, which, however, was not less than 1 hour in this instance. From the above results, compositization seemed to have completed by the curing for 1 hour at 70°C. Fig. 8 shows how hardness changed during the curing process, from which it is noted that hardness becomes greater as the temperature goes up higher until it reaches 70°C and as the curing time becomes longer. In the temperature range of over 70°C, an adverse result was observed. This may be attrib-

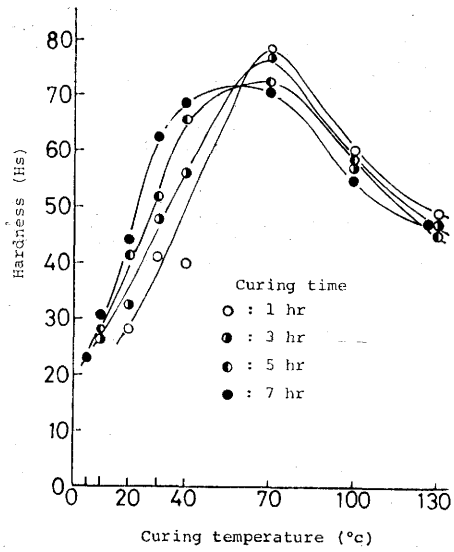


Fig. 8 Hardness change during the curing process.

utable to difference of curing of surface and inside, which difference is supposed to occur on account of different curing conditions. Relation between strength and hardness is shown in Fig. 9, from which it is observed that constant strength of 9–10 kg/mm² as FRP is expected when hardness reaches 40–50 (Hs), and that there exists a linear relation between hardness and strength within the above range, thus strength may be estimated from hardness. Relations in respect of mechanical properties of corrosion resistance and curing after temporary curing for 1 hour at 30°C are shown in Figs. 10–14. Fig. 10 shows relation between tensile strength and dipping time. It is noted from Fig. 10 that sulfuric-acid re-

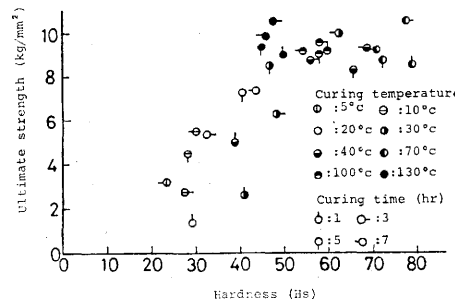


Fig. 9 Relation between strength and hardness.

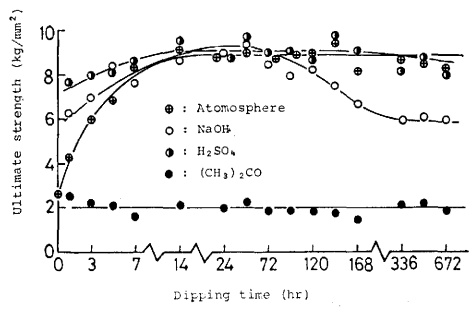


Fig. 10 Relation between tensile strength and dipping time.

sistance is not affected by dipping time. On the contrary, 48 hours are the limit to maintain curing so far as sodium-hydroxide resistance is concerned, and material beging to become brittle after that 48-hour limit by hydrolysis caused by attachment of ester, leading toward fall of strength. Acetone resistance was had, and strength was constant at 2kg/mm² irrespective of dipping time. This seems to be attributable to monocular chain at the end of incomplete cross linking being affected by acetone. Relation between strain at the time of breaking and dipping time is shown in Fig. 11, which resembles relation between tensile strength and dipping time. Fig. 12 shows elastic modulus, from which it is observed that tendency after 48 hours of dipping in sodium hydroxide differs from that shown in Figs. 10 and 11. It is observed as

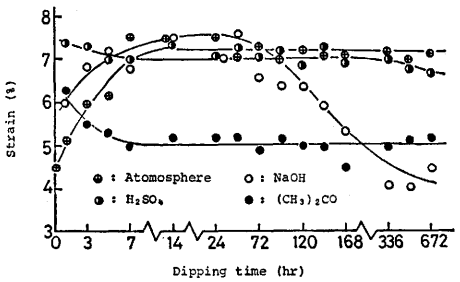


Fig. 11 Relation between strain at the time of breaking and dipping time.

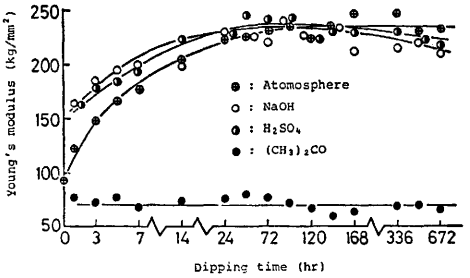


Fig. 12 Relation between young's modulus and dipping time.

well that, although stress and strain drop at the time of breaking, tangent is not affected, and the material deteriorate toward becoming brittle. Absorbed energy is shown in Fig. 13, which resembles Figs. 10 and 11. Fig. 14 shows relation between hardness and dipping time, and a problem is recognized to exist with respect to dipping in acetone and sodium hydroxide. Fracture caused by tension test was examined in the next place. Photos. 1-3 show fractures caused by tension of less than 3 kg/mm², 5-7 kg/mm² and 8 kg/mm² respectively, in which correlation between forms of composite bodies after fibers being removed and tensile strength is distinctly seen. Photo. 4 shows fractures caused by tension after 336 hours of dipping, and we can see how different corrosion liquids affect the material by comparing these fractures. (a) shows the material not dipped, while (b), (c) and (d) show materials dipped in sodium hydroxide, sulfuric acid and acetone, respectively. Layer of fibers is seen exposed in both (b) and (c). In (d), however, the fibers are observed to be separate, as if they are come off from the composite body, and it is obvious that they are no longer effective as reinforcement. Photo. 5 is the side view of Photo. 4. Fig. 15 is to see change of weight of specimens before and after dipping, from which it is noted that the ratio of weight change is greater when the curing temperature is higher. On the other hand, Fig. 16 shows change of weight after dipping and

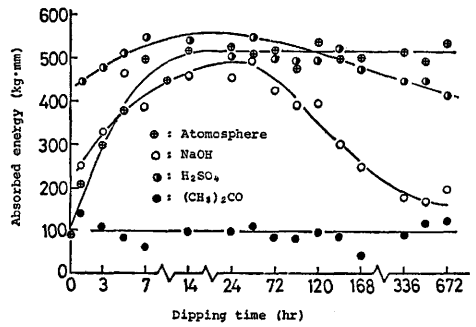


Fig. 13 Relation between absorbed energy and dipping time.

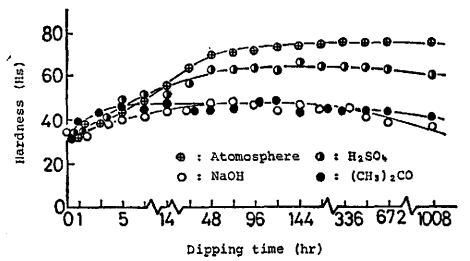


Fig. 14 Relation between hardness and dipping time.

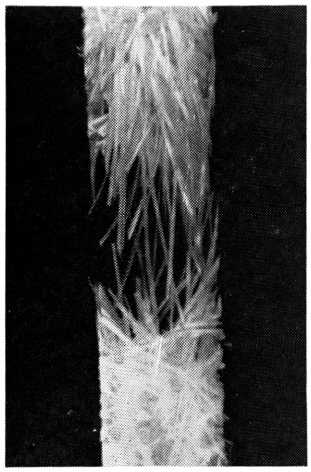


Photo. 1 Fracture caused by tension of less than 3 kg/mm^2.

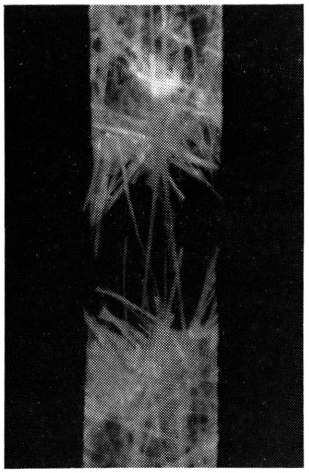
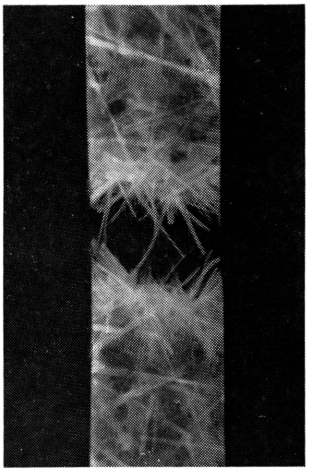


Photo. 2 Fracture caused by tension of less than 5~7kg/mm^2.

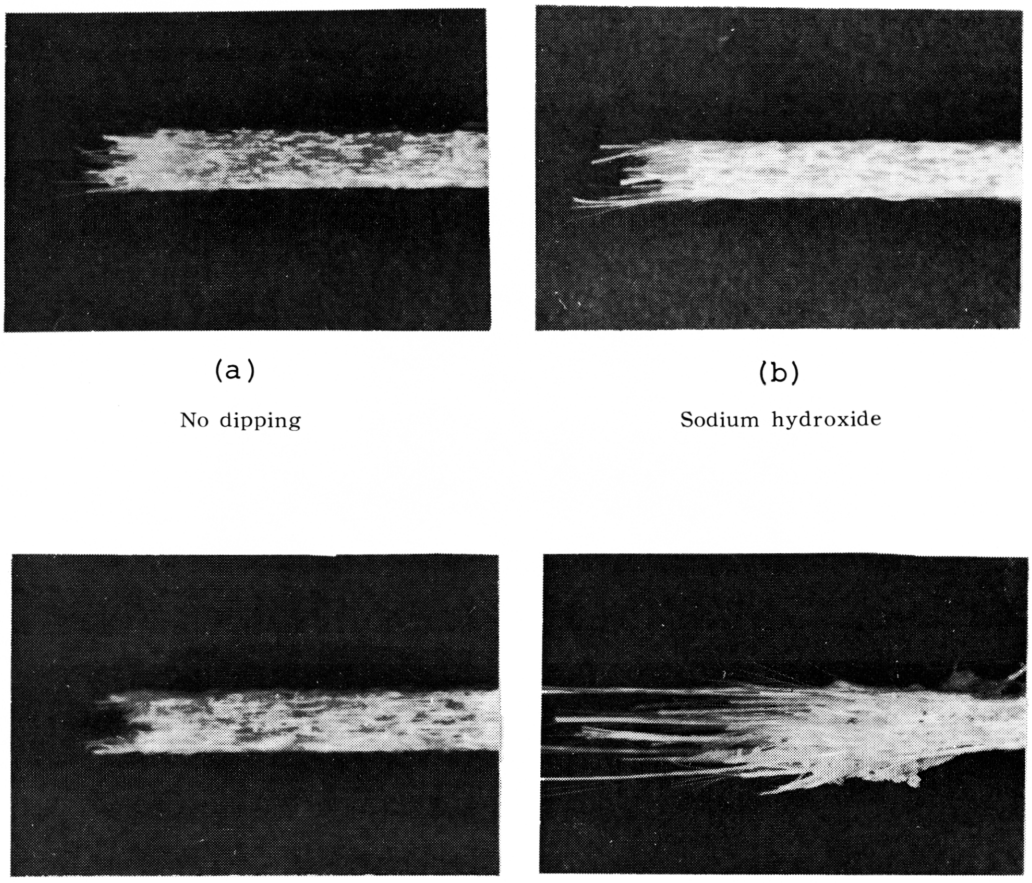


Rhoto. 3 Fracture caused by tension of less than 8 kg/mm^2.

(a) (b) (c) (d)

No dipping Sodium hydroxidc Sulfuric acid Acetone

Rhoto. 4 Fractures caused by tension after 336 hours of dipping.



(a) No dipping

(b) Sodium hydroxide

(c) Sulfuric acid

(d) Acetone

Photo. 5 Side view of fractures caused by tension after 336 hours of dipping.

after adjustment of conditions thereafter, and it is observed that weight change decreases sharply up to 70°C in curing temperature and then gradually goes up when curing temperature is over 70°C. Figs. 17 and 18 are to see change in weight before and after acid resistance test. Ratios of changes in length and thickness in sulfuric acid are shown in Figs. 19 and 20, from which it is observed that stable and favorable conditions could be attained in the neighborhood of 70°C. Similar tests were carried out with respect to acetone resistance, and the results are shwon in Figs. 21–24.

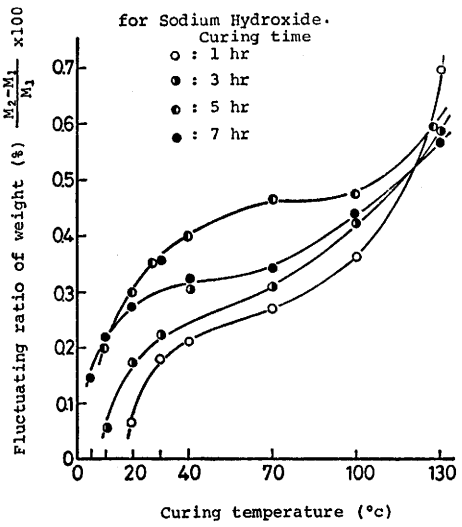


Fig. 15 Ratios in changes of weight of specimens before and after dipping.

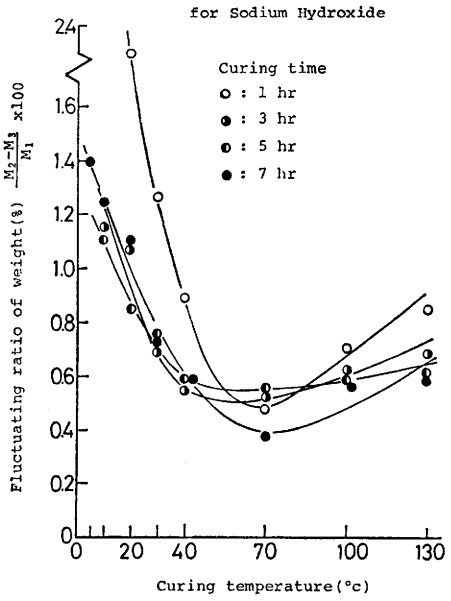


Fig. 16 Ratios in changes of weight after dipping and after adjustment of condition thereafter.

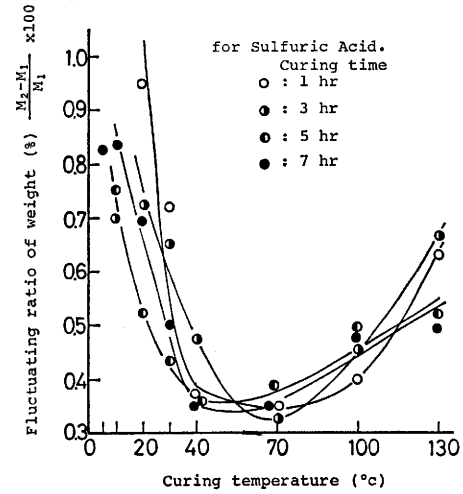


Fig. 17 Ratios in changes in weight before and after acid resistance test.

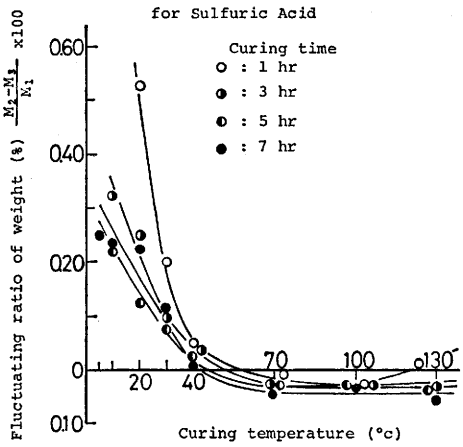


Fig. 18 Ratios in changes in weight after dipping in acid and after adjustment of conditions thereafter.

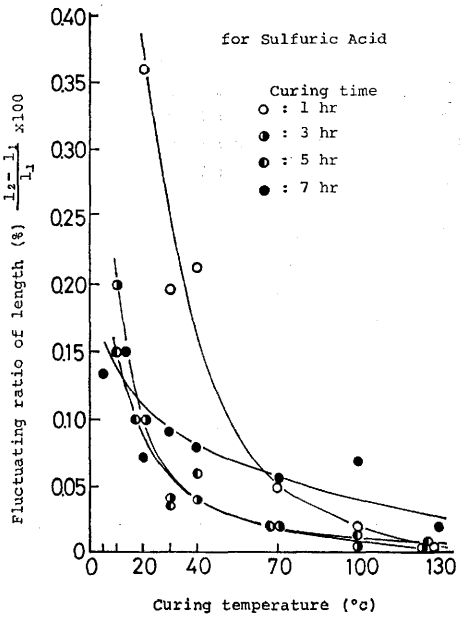


Fig. 19 Ratios of changes on length after dipping in sulfuric acid.

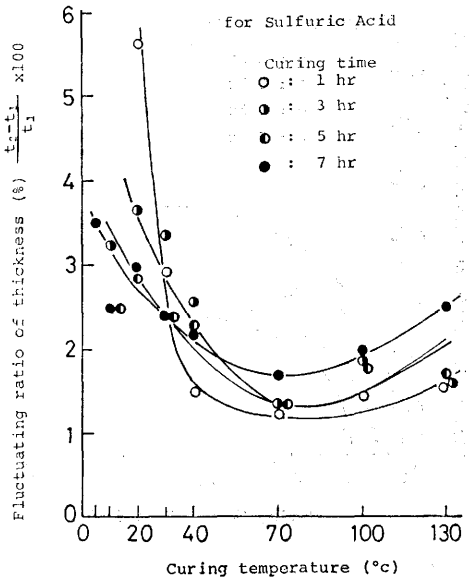


Fig. 20 Ratios of changes on thickness after dipping in sulfuric acic.

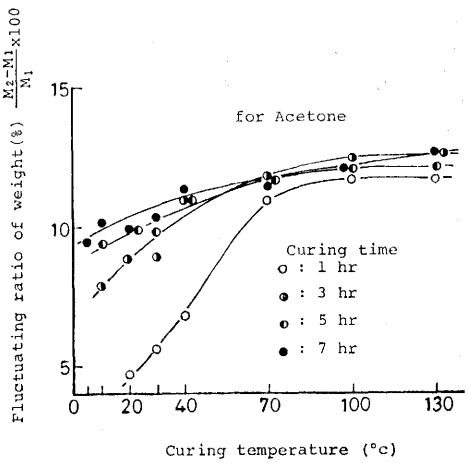


Fig. 21 Ratios of changes on weight after dipping in acetone.

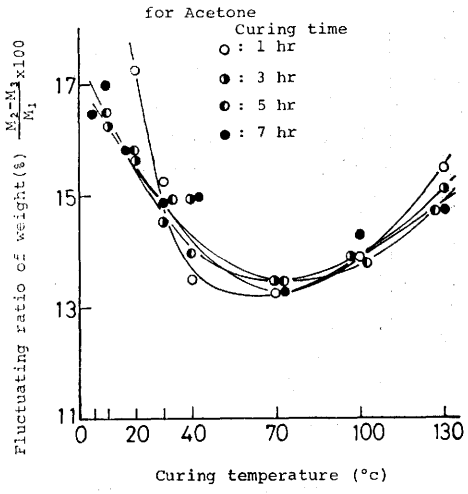


Fig. 22 Ratios of changes on weight after dipping and after adjustment of condition thereafter.

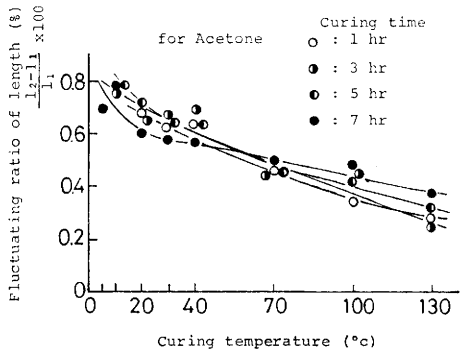


Fig. 23 Ratiaos of changes on length after dipping in acetone.

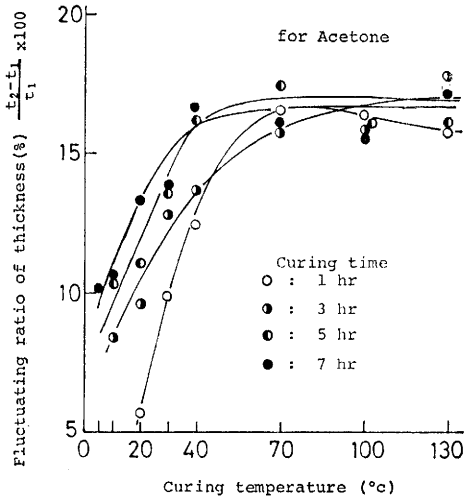


Fig. 24 Ratios of changes on thickness after dipping in acetone.

4. Conclusion

The following summary can be made from the results of the present experiments. As a result of this series of tests and experiments, it was found that a good composite body from the view points of properties, productivity and economy can be made through curing temperature of 70°C and curing time of 1 hour, and that such composite body had problems in resistance against acetone and sodium hydroxide, in spite of its good resistance against sulfuric acid. With regard to compositizing properties, over-curing was better and on the safer side than under-curing, but over-curing beyond the pertinent curing conditions did not make a contribution to betterment of properties.

Acknowledgments

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References

1) T. Hayashi: Engineering of composite materials (1971)
2) F. R. P Technical Association: F. R. P Hand book (1969)
3) H. Kimura: A study on the stress cracking, Memoirs of the Ehime University, Sect. III, Engineering Vol. VI, No. 1, p. 13 (1968)